Modern Physics

Unit 9: Statistical Laws of Nature
Lecture 9.1: Kinetic Theory of Gases

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Two reoccurring themes

Theme I: Behavior of $N$ particles

Theme II: Classical vs. Quantum statistics

Maxwell-Boltzmann

- no particles
- 1 particle
- 2 particles
- $N$ particles

Fermi-Dirac Bose-Einstein

- no particles
- 1 particle
- 2 particles
- $N$ particles
Theme I

- It is remarkable that science learned to deal with the properties of enormous numbers of particles BEFORE it discovered how to deal with individual atoms!

- The reason? Thermodynamic variables like pressure and temperature are AVERAGE values over $N$, a large number of particles.

- $N$ is a really large number, like $10^{23}$.

- Average values become very well defined and approach virtual certainty as $N \rightarrow \infty$
Study one gas molecule. Confine one air molecule into very narrow tube with moveable piston.

For elastic collision, magnitude of velocity does not change, so . . . .

\[ \Delta p_{\text{molecule}} = p_y(\text{final}) - p_y(\text{initial}) = -m|v_y| - (m|v_y|) = -2m|v_y| \]

ONLY one air molecule, mass \( m \), velocity \( +v_y \),

momentum \( p_y = mv_y \)

\[ \Delta t = \frac{2L}{|v_y|} \text{ roundtrip transit time} \]

Impulsive Force \( F = \frac{\Delta p}{\Delta t} \)

\[ F_A^y = \frac{F_{\text{av}}}{\Delta t} \]

What is \( F_{\text{av}} \)?
How to find average force value of N pulses in a time T?

Measure F at k discrete values and calculate an average:

\[ F_{av} = \frac{1}{k} \sum_{i=1}^{k} F_i \approx \frac{N F_o \Delta t}{T} = \frac{F_o \Delta t}{T/N} = \frac{F_o \Delta t}{\Delta t} = \left( \frac{\Delta p}{\Delta t} \right) \Delta t = \frac{\Delta p}{\delta t} \]

\[ F_{av} = \frac{\Delta p}{\delta t} \]
Evaluating the Average Force and Pressure

\[ F_{av} = \frac{\Delta p_{piston}}{\delta t} = \frac{2m|v_y|}{2L/|v_y|} = + \frac{m|v_y|^2}{L} \]

\[ P=\text{Pressure (one molecule)} = \frac{F_{av}}{A} = \frac{m|v_y|^2}{AL} = \frac{m|v_y|^2}{V} \]

\[ P = \frac{2*KE}{V} \]
Generalization to 3D: ONE gas molecule in a cylinder with a frictionless piston with area A

• when molecule hits wall, elastic collision
• collisions with **top** and **bottom** walls produces no change in magnitude or direction of \( v_x \), e.g.
  \[
  v_{\text{before}} = v_x \hat{i} + v_y \hat{j} + v_z \hat{k}
  \]
  \[
  v_{\text{after}} = v_x \hat{i} - v_y \hat{j} + v_z \hat{k}
  \]
• collisions with **left or right** wall reverses direction of \( v_x \)
  \[
  v_{\text{before}} = v_x \hat{i} + v_y \hat{j} + v_z \hat{k}
  \]
  \[
  v_{\text{after}} = -v_x \hat{i} + v_y \hat{j} + v_z \hat{k}
  \]
• no forces acting on molecule between collisions
For N non-interacting molecules, with identical mass, each with different velocity $v_{i,x}$ in x-direction

$$P(\text{total}) = \sum_{i=1}^{N} P_i = P = \sum_{i=1}^{N} \frac{mv_{i,x}^2}{V} = \frac{m}{V} \sum_{i=1}^{N} v_{i,x}^2$$

$$= \frac{Nm}{V} \left[ \frac{1}{N} \sum_{i=1}^{N} v_{i,x}^2 \right] = \frac{Nm}{V} \left[ v_{x,av}^2 \right]$$

Where $v_{x,av}$ is the average velocity in the x-direction.

$$PV = Nm[v_{x}^2]_{av} = 2N(\frac{1}{2} m [v_{x}^2]_{av})$$

x-direction only

How to calculate?

As N becomes very large, $[v_{x}^2]_{av}$ becomes well defined.
Molecular Interpretation of Temperature

• Comparing to Ideal Gas Law

\[ PV = N k_B T = 2N \left[ \frac{1}{2} m \left( \frac{v_x^2}{v_{av}} \right) \right] \]

\[ \frac{1}{2} m \left( \frac{v_x^2}{v_{av}} \right) = (KE_x)_{av} = \frac{1}{2} kT \]

• In general,

\[ \frac{1}{2} m \left( \frac{v_x^2}{v_{av}} \right) = (KE_x)_{av} = \frac{1}{2} kT \]

\[ \frac{1}{2} m \left( \frac{v_y^2}{v_{av}} \right) = (KE_y)_{av} = \frac{1}{2} kT \]

\[ \frac{1}{2} m \left( \frac{v_z^2}{v_{av}} \right) = (KE_z)_{av} = \frac{1}{2} kT \]

• but \( (v_x^2)_{av} = (v_y^2)_{av} = (v_z^2)_{av} \) (there’s nothing special about x-direction)

\[ 3 \left( \frac{v_x^2}{v_{av}} \right) = 3 \frac{v_x^2}{v_{av}} \]

\[ PV = N k_B T = 2N \left[ \frac{1}{2} m \frac{v_{av}^2}{3} \right] \Rightarrow k_B T = 2 \left[ \frac{1}{2} m \frac{v_{av}^2}{3} \right] \]

\[ \frac{1}{2} m \left[ \frac{\left( \frac{v_{av}^2}{3} \right)}{3} \right] = \frac{1}{2} k_B T \]

From this result we infer that

\[ KE_{av} = K_{av} = \frac{1}{2} m \left( \frac{v_{av}^2}{v_{av}} \right) = \frac{3}{2} k_B T \ (for \ one \ molecule) \]
Estimating the average speed in a gas of N particles

\[ K_{tot} = N \left[ \frac{1}{2} m (v^2)_{av} \right] = \frac{3}{2} N k_B T \]

\[ (v^2)_{av} = \frac{3 k_B T}{m} = \frac{3 \left( N_A k_B \right) T}{N_A m} = \frac{3RT}{M} \]

\[ v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3RT}{M}} \]

[Note that \( v_{rms} = (v^2)_{av} \)]
How could you better characterize a gas of \( N \) atoms in equilibrium at temperature \( T \)?

Two Choices

**A. List of numbers**

At some \( t = t_1 \)

Particle 1: \( r_1 \quad v_1 \quad E_1 \)

Particle 2: \( r_2 \quad v_2 \quad E_2 \)

Particle 3: \( r_3 \quad v_3 \quad E_3 \)

\[ \cdots \]

Particle \( N \): \( r_N \quad v_N \quad E_N \)

\(<K_{av}> = \frac{3}{2} k_B T\)

**B. Probability Distribution**

from equipartition theorem, we know that each molecule has (on average) \( \frac{3}{2} k_B T \) of KE.
Up Next – the Maxwell-Boltzmann Distribution function
Appendix: Make sure you understand why an “rms” value might be preferred over an “average” value.

Given five numbers: \( N = \{5, 11, 32, 67, -89\} \)

\[
N_{\text{av}} = \langle N \rangle = \frac{5 + 11 + 32 + 67 + (-89)}{5} = 5.2
\]

\[
(N^2)_{\text{av}} = \langle N^2 \rangle = \frac{5^2 + 11^2 + 32^2 + 67^2 + (-89)^2}{5} = 2716
\]

\[
N_{\text{rms}} = \sqrt{(N^2)_{\text{av}}} = \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + (-89)^2}{5}} = 52.1
\]

Focus on the “rms” value compared to \( N_{\text{av}} \)

For the five numbers listed, \( N_{\text{av}} \) gives a misleading (low) result because the large negative number (-89) skews the calculation. The value for \( N_{\text{rms}} \) more accurately represents the magnitude of the original five numbers specified.